

12p.  
N64-28752

## Amorphous Phosphate Coatings for Thermal Control of Echo II

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Code Name

Cat-28752

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The absorptance and emittance characteristics of some amorphous phosphate coatings applied to an aluminum-foil substrate have been investigated to determine their usefulness as thermal control coatings for the NASA Echo II satellite. The spectral absorptance was measured over the range 0.22-15 $\mu$  and the total hemispherical emittance was determined for specimen temperatures in the range 0°-100°C for coating surface densities up to 400 mg/ft<sup>2</sup>. The equilibrium temperature control parameter,  $\alpha_s/\epsilon$ , varies over the range 7.5-0.82 for the surface densities investigated. The thermal radiation stability of the coating is presented for periods up to 1250 hr in a simulated space environment.

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Ordinarily, the most significant parameter that can be varied to control the temperature of satellites and space vehicles is the ratio of the solar absorptance to the low-temperature emittance ( $\alpha_s/\epsilon$ ) of the external surface. At the present time, passive thermal control techniques are generally employed to maintain the spacecraft temperature within tolerable limits.

The choice of available passive coatings is restricted to a considerable extent by the inability of many commonly available surface coatings to withstand the effects of the space environment. It is fairly practical to study the effects of high vacuum, heat and ultraviolet radiation since these can be simulated to a reliable degree in the laboratory, but the effects of bombardment by micrometeoroids and by atomic, molecular, ionic and fundamental particles are less easily investigated. In any case, a large variety of materials and coatings are being investigated by various research organizations in order to develop coatings which will have stable thermal radiation characteristics in the space environment. These include organic and inorganic paints, enamels, ceramics, stably oxidized metals and vapor-deposited and electrodeposited metals.

Generally, weight is not a major consideration in selecting the required thermal control coating. However, in certain applications, it can become quite important as in the case of large, thin-wall, passive communications satellites of the Echo type, where the mass-to-area ratio of the structure is quite small. In such cases, the coating weight could easily become an appreciable portion of the total satellite weight. The extremely large surface area of such satellites makes it highly desirable that the thermal control coating be applied to the base material in a mass-production process before the material is cut into the proper-shaped sections for balloon construction. The long-lifetime requirements of such satellites suggest that an inorganic type of coating would be preferable to an organic type since the latter tends to deteriorate more rapidly with consequent changes in its thermal radiation characteristics when subjected to the space environment.

The above factors were carefully considered in the choice of a thermal control coating for the

NASA Echo II<sup>1</sup> satellite, which will be a 135-ft-diam passive communications sphere constructed of a three-layer laminate composed of a 0.00035-in.-thick Mylar film adhesively bonded between two layers of 0.00018-in.-thick, 1080 aluminum foil. The aluminum foil has a low-temperature (0°-100°C) emittance of 0.03 and absorptance to solar radiation of 0.18, giving it an  $\alpha_s/\epsilon$  ratio of 6.0. It was desirable to alter the aluminum surface characteristics such that an  $\alpha_s/\epsilon$  ratio of 1.67 would be obtained. There are essentially three approaches that can be taken to obtain this characteristic, namely, 1—find a material that has an  $\alpha_s/\epsilon$  ratio of exactly 1.67 and deposit it on the aluminum-foil substrate; 2—select a material that has a much lower  $\alpha_s/\epsilon$  value than 1.67 and partially coat the sphere, in a dot pattern of some form, to such an extent that the effective  $\alpha_s/\epsilon$  ratio of 1.67 is obtained; 3—select a coating that has an  $\alpha_s/\epsilon$  value less than 1.67 and apply it on the aluminum foil to such thickness that the resulting  $\alpha_s/\epsilon$  will be 1.67. This last, third, approach was used in producing the desired thermal characteristics for the NASA Echo II satellite because the

<sup>1</sup> The Echo II satellite is being developed as part of the NASA designated Echo A-12 project.

<sup>2</sup> Trade name of coatings as prepared by The Amchem Products Co.

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quality control could be better maintained and the weight penalty would be minimized.

A method was developed a few years ago for coating the surface of aluminum with an amorphous phosphate film of controllable thickness or surface density. This process is referred to commercially as "Alodizing" and the solution used for the chemical conversion of the aluminum surface is referred to commercially as "Alodine."<sup>2</sup> Alodine is primarily used as a paint bonding and underpaint corrosion-inhibiting coating for aluminum and aluminum alloys. Ref. (1) reports the following as some of the properties of Alodine: 1—the coating may be applied by immersion, spraying or brushing; 2—it forms a relatively hard, dense, nonporous coating, yet it is as flexible as aluminum itself and, when properly applied, it may be heated to the melting point of aluminum without material change in its protective or paint bonding properties; 3—it appears that the coatings have a relatively high electrical resistance which increases rapidly with coating thickness and offers protection against bimetallic or galvanic corrosion; 4—the Alodine solution consists of a mixture of chromic, phosphoric and hydrofluoric acids in proportions which vary according to the type of Alodine; 5—chemical and spectrographic analysis of a typical coating indicate that it contains 18-20% Cr, 4-5% Al, 15-17% P and 0.2% F, in addition to some oxygen, hydrogen, calcium and perhaps alloying elements from the aluminum base metal. The main constituents are assumed to be 50-55%  $\text{CrPO}_4$ , 17-23%  $\text{AlPO}_4$ , 22-33% water (the water can be wholly or partially driven off by heat). There may also be traces (less than 0.5%) of fluorides of aluminum, chromium and calcium; 6—the solubility of the coating depends on the per cent moisture content and, hence, the drying temperature and aging process. In general, the coating is insoluble in  $\text{H}_2\text{O}$ , alcohol, solvents, most dilute acids and alkalis. It is soluble in molten sodium nitrate and slightly soluble in concentrated nitric acid.

#### Determination of Solar Absorptance

**Apparatus.**—For purposes of convenience, two different ratio-recording spectrophotometers with integrating sphere attachments were used for measuring the total spectral reflectance of the test specimen relative to that of a magnesium oxide surface. A conventional Beckman DK-1 instrument was used for making all reflectance scans of Alodine 1200S and 401-41, and a model 14 Cary instrument was used to investigate the spectral reflectance of Alodine 401-45. Dual light sources were employed for covering the spectral range from 0.22 to  $2.6\mu$  with the Beckman DK-1 and 0.22 to  $2.1\mu$  with the Cary 14. These wave length intervals include 97 and 95% of the solar energy, respectively. The test specimens were adhesively bonded to  $\frac{1}{8}$ -in.-thick flat machined disks for mounting into the instruments.

**Measurements.**—The spectral reflectance ( $r_\lambda$ ) can be related to the spectral absorptance ( $\alpha_\lambda$ ) by the expression

$$\alpha_\lambda = 1 - r_\lambda \quad [1]$$

for materials that are opaque as they are in this case.

The value of the total solar absorptance can be obtained from the expression (2)

$$\alpha_s = \frac{\int_0^\infty \alpha_\lambda S_\lambda d\lambda}{\int_0^\infty S_\lambda d\lambda} \quad [2]$$

where  $S_\lambda$  is the monochromatic intensity of the solar radiation outside the earth's atmosphere incident on a surface normal to the sun's rays at the mean earth-sun distance. However, due to the finite wave length range over which the spectral analysis was made, the following expression was used to determine the solar absorptances of the surface coatings reported herein:

$$\alpha_s = \frac{\int_{0.22\mu}^{\lambda_{\max}} \alpha_\lambda S_\lambda d\lambda}{\int_{0.22\mu}^{\lambda_{\max}} S_\lambda d\lambda} \quad [3]$$

where  $\lambda_{\max} = 2.6\mu$  for the Beckman DK-1 data and  $2.1\mu$  for the Cary 14 data, thereby limiting the evaluation to 97 and 95% of the solar energy, respectively. The absorptance data presented herein have been corrected for the finite absorption of the magnesium oxide reference plate (3).

#### Determination of Low-Temperature Emittance

**Apparatus.**—The study of low-temperature emittance characteristics included herein have been accomplished with the aid of two instruments. A conventional Perkin-Elmer model 13 ratio-recording infrared spectrophotometer with reflectance attachment was used to measure the total normal spectral reflectance of specimens for study of band structure.

A specially designed apparatus was used to measure the total hemispherical emittance of the test specimens. It consists essentially of two coaxial cylinders as shown in Fig. 1. The outer cylinder will be referred to as the cooled cylinder and the inner cylinder as the heated cylinder or tube. This apparatus is designed for investigating the low-temperature emittance of thin-film or foil-type materials that can be tightly bonded to the heated cylinder.

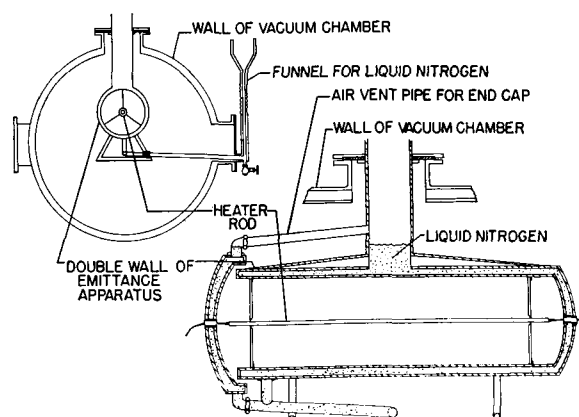


Fig. 1. Cross sections of vacuum chamber and emittance apparatus

der. Investigations may also be made of the emittances of materials that can be vapor-deposited or painted on the outside surface of the heated cylinder if they are of sufficient thickness to be opaque in the infrared.

The outer cylinder has a double wall made of stainless steel. It is 50 in. long with an inside diameter of 12 in. It fits inside a 5-ft-long vacuum tank that will maintain pressures at less than  $10^{-6}$  torr where air conductive and convective heat transfer can be neglected (4). The double wall characteristic permits cooling of the surface to liquid nitrogen temperature. The liquid nitrogen is loaded through the funnel arrangement shown in Fig. 1 and is gravity fed through the vacuum tank wall and into the double-wall cavity of the cooled cylinder where it is vented to the atmosphere through the support column attached to the top porthole of the vacuum tank. The outside surface of the cooled cylinder is polished so that the absorption of radiation from the surrounding environment is minimized and the inside surface is painted with a flat black enamel (absorptance  $\geq 0.95$ ) to give maximum absorptance in the infrared. One end of the cooled cylinder is removable so that the test specimen can be changed. It will be noticed in Fig. 1 that the removable end is oversized so that the inside of the cylinder can be evacuated and that it wraps around the end of the cylindrical section to form an optical baffle so that the radiation exchange between the inside and outside of the cylinder is minimized.

The heated cylinder consists of a  $\frac{5}{8}$ -in.-OD Inconel tube. This tube is supported along the axis of the cooled cylinder by means of a low thermal conductivity, three-spoke arrangement as shown in Fig. 1. The Inconel tube is directly heated by passing alternating current through it. The temperature of the tube is monitored by passing twelve 36-gauge copper-constantan thermocouples up through the inside of the tube and embedding them in the tube wall. The leads used to supply the heating current, as well as the thermocouple leads, pass out through a small hole in each end of the cooled cylinder. Guard heaters are wound on each end of the Inconel tube just inside the tube support positions to compensate for heat losses by conduction through the supports and heater current wiring.

The heated cylinder is shown in Fig. 2 removed from the cooled cylinder and a test specimen of Alodine-coated Echo II material partially installed. The laminate is adhesively bonded to the outside surface of the Inconel tube with a very thin layer of thermosetting resin so that no appreciable temperature variation can exist between the radiating surface of the laminate and the Inconel tube. The emittance measurements were made at three temperatures near  $0^\circ$ ,  $50^\circ$  and  $100^\circ\text{C}$ .

**Measurements.**—The total normal spectral reflectance ( $r_{\lambda,N}$ ) obtained by use of the Perkin-Elmer model 13 spectrophotometer is related to the total normal spectral absorptance ( $\alpha_{\lambda,N}$ ) by

$$\alpha_{\lambda,N}(T) = 1 - r_{\lambda,N}(T) \quad [4]$$

when none of the incident radiation is transmitted.

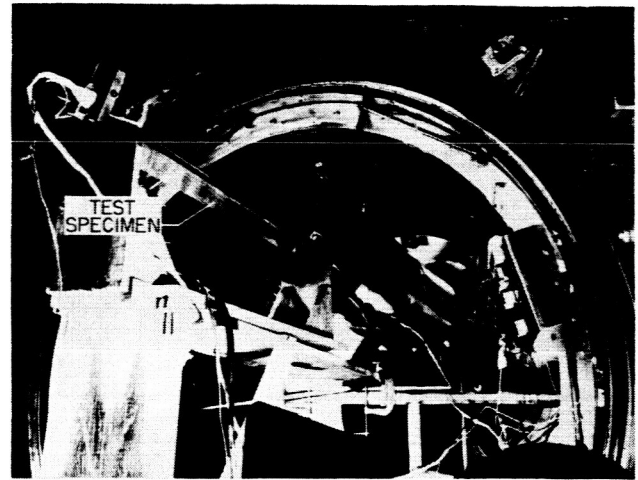


Fig. 2. Emittance apparatus with sample tube withdrawn and test sample partially mounted.

Since the spectral absorptance and emittance of a material at a given temperature are equal (5), Eq. [4] can be rewritten as

$$\epsilon_{\lambda,N}(T) = 1 - r_{\lambda,N}(T) \quad [5]$$

The total normal emittance of a material at a given temperature [ $\epsilon_N(T)$ ] can be calculated from the spectral reflectance data by use of the equation

$$\epsilon_N = 1 - \frac{\int_{\lambda=0}^{\lambda=\infty} r_{\lambda,N}(T) J_{\lambda}(T) d\lambda}{\int_{\lambda=0}^{\lambda=\infty} J_{\lambda}(T) d\lambda} \quad [6]$$

where  $J_{\lambda}(T)$  is the monochromatic emissive power of a black body expressed by Planck as

$$J_{\lambda} = C_1 \lambda^{-5} \left[ \exp \left( \frac{C_2}{\lambda T} \right) - 1 \right]^{-1} \quad [7]$$

Eq. [6] is used herein for the explicit purpose of evaluating environmental effects on the emittance of the coatings in the spectral range of 2-15 $\mu$ .

The method of determining the total hemispherical emittance  $\epsilon(T)$  of materials using the specially designed apparatus follows from an analysis of the radiative heat exchange between two coaxial cylinders (6). The expression for the rate of net radiative heat exchange between the inner and outer cylinder is

$$\frac{dq}{dt} = \sigma A_1 \frac{1}{\frac{1}{\epsilon_1} + \frac{A_1}{A_2} \left( \frac{1}{\epsilon_2} - 1 \right)} (T_1^4 - T_2^4) \quad [8]$$

where

- $\sigma$  = Stefan-Boltzmann constant
- $A$  = surface area
- $\epsilon$  = total hemispherical surface emittance
- $T$  = absolute temperature

and the subscripts 1 and 2 refer to the inner and outer surface, respectively. In Eq. [8]

$$\frac{A_1}{A_2} \left( \frac{1}{\epsilon_2} - 1 \right) \ll \frac{1}{\epsilon_1}$$

for the apparatus described, even when the emittance of the test specimen ( $\epsilon_1$ ) is 1.0, so the second

term in the denominator of Eq. [8] can be set equal to zero for simplicity. By maintaining the temperature of the outside cylinder at liquid nitrogen temperature ( $T_2 = 78^\circ\text{K}$ ), the  $T_2^4$  term becomes quite small compared to  $T_1^4$ .

$$T_2^4 \leq 0.006T_1^4 \text{ for } T_1 \geq 273^\circ\text{K}$$

therefore,  $T_2^4$  also is set equal to zero. Eq. [8] can now be written as

$$\frac{dq}{dt} = \epsilon_1 \sigma T_1^4 A_1 \quad [9]$$

for determining the emittance of specimens at temperatures of  $0^\circ\text{C}$  and above. This equation gives the radiative heat output from a gray body that has a total hemispherical emittance of  $\epsilon_1$  while maintained at a temperature of  $T_1$ . By measuring the rate of heat radiated and the temperature of the body, the emittance can be determined. With the emittance apparatus described, the rate of radiative heat loss is equal to the electrical power dissipated by the tube, assuming no losses occur through conduction or radiation out of the ends of the tube while the temperature of the tube is stabilized at  $T_1$ , that is

$$EI = \epsilon_1 \sigma T_1^4 A_1 \quad [10]$$

from which

$$\epsilon_1 = \frac{EI}{\sigma T_1^4 A_1} \quad [11]$$

where  $E$  is the voltage drop across the test section and  $I$  is the current through the tube. The test section referred to is the center 22 in. of the heated tube shown in Fig. 3(a) where the location of the temperature monitoring thermocouples is also indicated. A small lead is passed through each end of the tube and embedded in the wall at each end of the test section for the purpose of monitoring the voltage drop " $E$ " across the test section while passing a current " $I$ " through it. There were large conduction losses at the ends of the heated tube through the support structure to the cooled cylinder so that, for example, the temperature toward the ends of the tube dropped toward  $0^\circ\text{C}$  when the middle of the tube was  $50^\circ\text{C}$  as shown in Fig. 3(b). To eliminate this nonuniformity, a guard heater was placed on each end of the tube, supplied from an independent variable power source that could be ad-

justed until the temperature was uniform along the test section of the tube as shown in Fig. 3(c). No thermal conduction out of the test section toward the ends of the tube will then occur since no temperature variation is present. Radiative heat losses from the inside of the tube were made negligible by extending the ends of the tube about 10 in. beyond the test section. It is estimated that the total hemispherical emittance values measured with this apparatus have an uncertainty of about 6%.

### Preparation of Test Specimens

Alodine coatings were applied to the Echo II 1080 aluminum-foil Mylar laminate by an immersion process for evaluation. The immersion process was selected because of its utility in coating the material in a mass production operation. The enormous size of an Echo II sphere can be seen in Fig. 4 with a model of the oblate spheroid canister into which it will be packaged for flight seen in the foreground. Since the laminate is fabricated in strips about 54 in. wide and a few hundred yards long and supplied in rolls, it lends itself very well to the immersion process where it can be pulled through a vat of the solution and the immersion time controlled by the speed of the takeup roller.

The test specimens were first cleaned to remove all oil film and other foreign material with an inhibited mild alkali referred to commercially as "Ridoline 106". They were then immersed in a vat containing the Alodine solution for various periods of time to establish the coating weight variation with immersion time for the particular solution concentration and temperature. The specimens were then removed from the Alodine solution and rinsed with water. Next, the specimens were dried for a short period of time and the coating weight determined. The times required to deposit various types of Alodine are shown in Fig. 5. The Alodine 1500 is seen to deposit at a comparatively slow rate so that it may have created an application problem; therefore, it was not investigated further. The Alodine 410 deposited at such a rapid rate that it would tend to make the immersion time quite critical and difficult to control; hence, it was also discarded. The

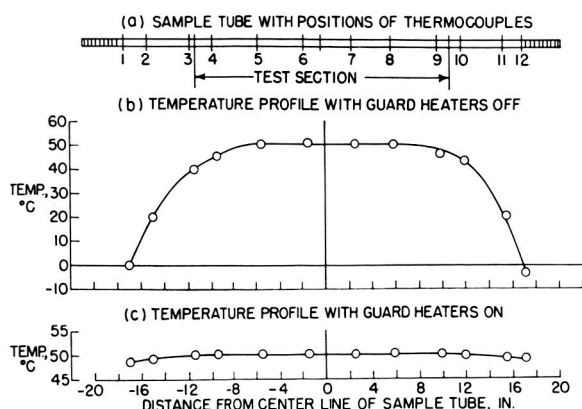


Fig. 3. Temperature profile of sample tube and positions of thermocouple attachments.



Fig. 4. Echo II, 135 ft in diameter

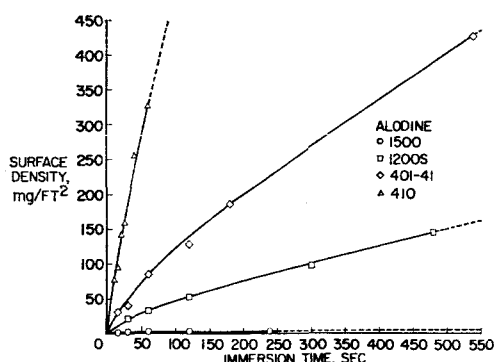


Fig. 5. Variation of surface density with immersion time in Alodine solution.

Alodines 1200S, 401-41 and 401-45, which deposit at intermediate rates, were selected for evaluation as thermal control coatings.

### Results and Discussion

**General Thermal Radiation Characteristics.**—A compilation of the various thermal radiation characteristics of the Alodines 1200S, 401-41, and 401-45 is shown in Table I. The temperature of the specimens was maintained at approximately room temperature (25°C) while the absorptances were being measured. The total hemispherical emittances were measured at three different temperatures between 0° and 100°C. The temperature controlling parameter ( $\alpha_s/\epsilon$ ) was calculated for 50°C since this value is more representative of space vehicle temperatures. In particular, the Echo II satellite will have attached to its surface two radio beacons that will not operate satisfactorily above about 70°C and it will also contain an inflation system that will not operate satisfactorily below about 45°C.

The variation of spectral absorptance with surface density for Alodine 1200S is shown in Fig. 6 for coating weights up to 143 mg/ft². The spectral absorptance of the uncoated aluminum-foil substrate is shown for comparison. It is seen that with a very thin coating (16.8 mg/ft²) the absorptance is tremendously increased in the near ultraviolet portion of the spectrum but increases only about 50-100% in the spectral range  $0.7\mu \leq \lambda \leq 2.6\mu$ . As the coating density is increased, the absorptance increases in the interval  $0.2\mu \leq \lambda \leq 0.75\mu$  but remains about the same in the interval  $0.75\mu \leq \lambda \leq 2.6\mu$ .

The variation of spectral absorptance with surface density for Alodine 401-41 is shown in Fig. 7 for coating weights up to 426 mg/ft². The spectral absorptance in the near ultraviolet is quite pronounced; however, it decreases rather rapidly in the interval  $0.22\mu \leq \lambda \leq 0.35\mu$  showing two absorption bands peaking at 0.42 and 0.62 $\mu$ . These absorption bands become quite well pronounced for coating weights of 426 mg/ft². It is noted that the absorptance generally increases with increasing coating weights in the interval  $0.22\mu \leq \lambda \leq 0.94\mu$  and decreases with increasing coating weight in the interval  $0.94\mu \leq \lambda \leq 2.6\mu$ . This partially explains the rather constant absorptance to solar radiation calculated for this coating even though the coating weights vary over a large range, as shown in Fig. 8.

Table I. Alodine thermal characteristics

Alodine	Immersion time (sec)	Surface density, mg/ft²	Temp, °C	$\epsilon$	$\alpha_s$	$\alpha_s/\epsilon$
1200S	15	30.4	-2	0.0410	0.331	7.12
			48	0.0465		
			94	0.0460		
	30	40.0	2.7	0.0520	0.357	6.05
			57	0.059		
			97	0.059		
			0	0.071		
	60	83.2	44	0.082	0.343	4.18
			96	0.087		
			2	0.148		
401-41	120	141.2	47	0.158	0.349	2.21
			95	0.156		
			-2	0.159		
	180	184	54	0.180	0.335	1.86
			96	0.181		
			-1	0.202		
	240	300	50	0.262	0.347	1.32
			92	0.252		
			-2	0.506		
	540	426	50	0.506	0.414	0.82
			93	0.505		
401-45	—	122	-0.5	0.102	0.321	2.72
			51	0.118		
			97	0.120		
	—	155	-1.0	0.124	0.338	2.60
			51	0.130		
			96	0.135		
	—	172	0	0.155	0.340	2.12
			50	0.160		
			97	0.184		
	—	193	1	0.178	0.345	1.97
			50	0.175		
1200 S	—	222	97	0.175	—	—
			1	0.185		
			50	0.202		
	—	250	97	0.203	—	—
			0	0.213		
			51	0.224		
	30	20.6	95	0.219	0.395	8.59
			6	0.047		
			58	0.046		
	60	32.4	90	0.046	0.432	8.31
			2	0.043		
1200 S	—	51.6	52	0.052	0.480	7.50
			93	0.049		
			-5	0.070		
	300	96	57	0.064	0.487	6.96
			98	0.061		
			2	0.077		
	480	143	51	0.070	0.488	5.19
			97	0.073		
			4	0.101		
	—	—	46	0.094		
			91	0.094		

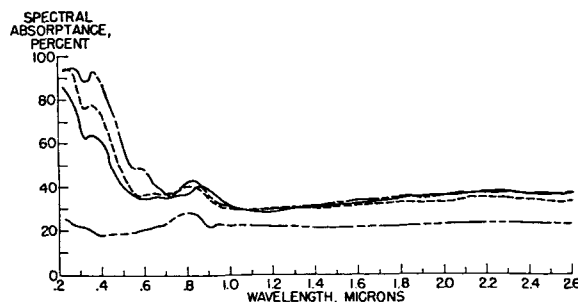


Fig. 6. Variation of spectral absorptance with surface density for Alodine 1200S: — 16.8 mg/ft² (1200S), - - - 70.0 mg/ft² (1200S), - · - 143 mg/ft² (1200S), · · · aluminum foil substrate.



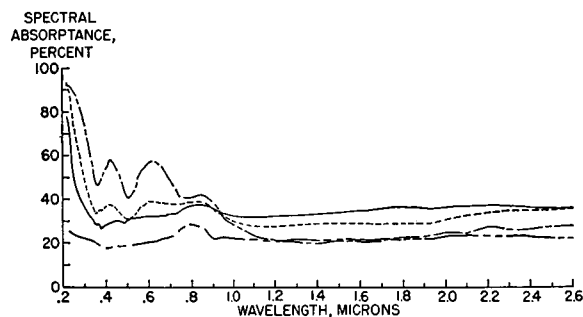


Fig. 7. Variation of spectral absorbance with surface density for Alodine 401-41: — 30.4 mg/ft<sup>2</sup> (401-41), - - - 300 mg/ft<sup>2</sup> (401-41), - · - 426 mg/ft<sup>2</sup> (401-41), · · · aluminum foil substrate.

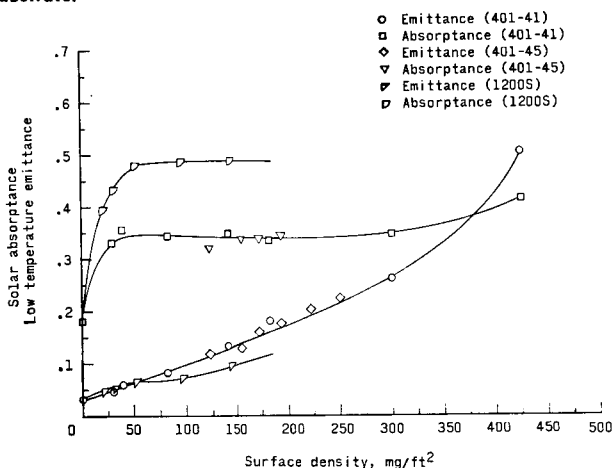


Fig. 8. Variation of solar absorbance and low-temperature emittance with surface density for Alodines 1200S, 401-41 and 401-45.

The total solar absorbance as determined from

$$\bar{T} = \sqrt[4]{\frac{S\alpha_s}{4\sigma\epsilon_0} \left\{ 1 + 2 \left( aF_R + \frac{1-a}{4} \frac{\epsilon_0}{\alpha_s} \right) [1 - (1-k^2)^{1/2}] \right\}} \quad [12]$$

Eq. [3] and the hemispherical emittance (at  $\approx 50^\circ\text{C}$ ) as determined from Eq. [11] are shown in Fig. 8 for the coating densities investigated. The absorbance of solar radiation for the Alodine 401-41 is seen to increase from that of the aluminum-foil substrate ( $\alpha_s = 0.18$ ) to about 0.33 as the coating density increases from 0 to about 50 mg/ft<sup>2</sup> and remains rather constant at this value as the coating density increases further from 50 to 300 mg/ft<sup>2</sup>; however, a slight increase appears at the end of the curve and the absorbance reaches 0.41 at a coating density of 426 mg/ft<sup>2</sup>. The emittance, however, increases continually with increasing coating density, reaching a value of about 0.50 at 426 mg/ft<sup>2</sup>. The absorbance and emittance of Alodine 401-45 were measured over the range of 122-250 mg/ft<sup>2</sup> and within these limits have approximately the same characteristics as Alodine 401-41 (Fig. 8). The solar absorbance of Alodine 1200S increases from that of the aluminum-foil substrate to about 0.48 as the coating density increases from 0 to 90 mg/ft<sup>2</sup> and remains rather constant with further increase in density. Its emittance increases from that of the aluminum-foil substrate ( $\epsilon = 0.03$ ) to about 0.095 for a 142-mg/ft<sup>2</sup> coating and probably continues to increase with coating density as it did for the 401-41 and 401-45.

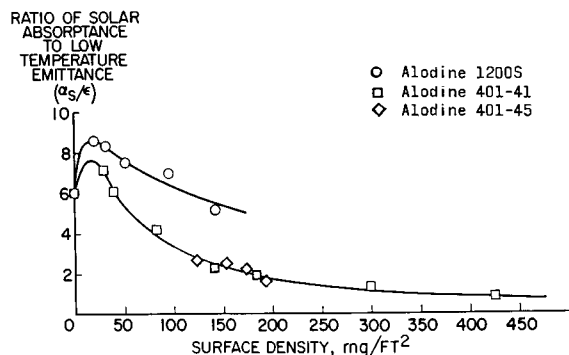


Fig. 9. Variation of  $\alpha_s/\epsilon$  with surface density for Alodines 401-41, 401-45 and 1200S.

The variation of the satellite temperature control parameter ( $\alpha_s/\epsilon$ ) is shown in Fig. 9 for Alodines 1200S, 401-41 and 401-45 as the coating densities are increased. The  $\alpha_s/\epsilon$  value is seen to increase rather sharply for the Alodine 1200S, reaching a value of 8.6 for a coating density of about 15 mg/ft<sup>2</sup>, then decreasing to 5.5 at a coating weight of about 160 mg/ft<sup>2</sup>. The  $\alpha_s/\epsilon$  ratio for Alodine 401-41 also increases at first, reaching a value of about 7.5 at 20 mg/ft<sup>2</sup>, but then decreases, rapidly at first, then tending to become constant about 0.82 for coating densities above about 425 mg/ft<sup>2</sup>. The  $\alpha_s/\epsilon$  values of Alodine 401-45 are seen to be quite comparable to those of 401-41 within the limits of surface density investigated.

**Thermal Control.**—The effects of the wide range  $\alpha_s/\epsilon$  values on the passive temperature control of Echo-type satellites can be seen from the relation (7)

where

- $\bar{T}$  = satellite equilibrium mean temperature in sunlight
- $S$  = solar radiation constant
- $\alpha_s$  = absolute total solar absorbance of satellite surface
- $a$  = earth albedo
- $F_R$  = geometric view factor for albedo radiation
- $\epsilon_0$  = total hemispherical emittance of satellite outside surface
- $k = \frac{R_E}{R_E + h}$
- $R_E$  = radius of earth
- $h$  = orbital altitude

To illustrate the relation between the equilibrium temperature and the  $\alpha_s/\epsilon$  value, a satellite orbit is selected such that its plane is normal to the sun's rays ( $F_R \approx 0.07$ ) and 1000 nautical miles in altitude. If the  $\alpha_s/\epsilon$  value of the satellite's outside surface should change as a result of the space environment, the equilibrium temperature will change accordingly. A family of curves are included in Fig. 10 which gives the predicted relations between  $\alpha_s/\epsilon$  and equilibrium temperature. The central curve (0 change) is for a perfectly stable coating and the

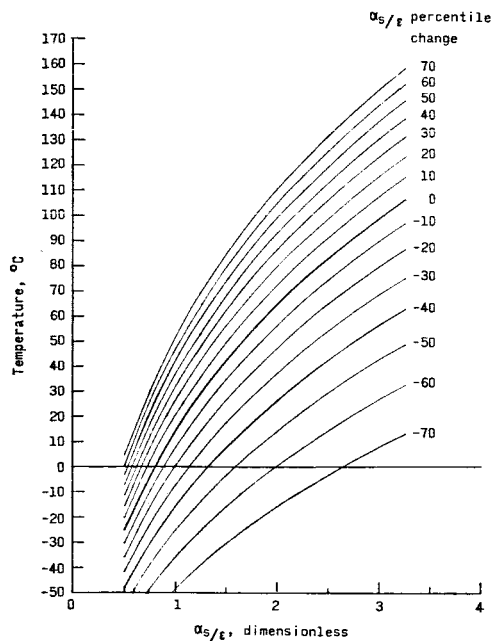


Fig. 10. Equilibrium temperature vs.  $\alpha_s/\epsilon$  value for 1000 nautical miles' altitude and temperature changes resulting from various percentile changes in initial  $\alpha_s/\epsilon$  value.

other curves illustrate the equilibrium temperature that would result from various percentile changes in the initial  $\alpha_s/\epsilon$  value. For example, a satellite that has an initial  $\alpha_s/\epsilon$  ratio of 1.5 will reach thermal equilibrium at 42°C; if the  $\alpha_s/\epsilon$  value should increase 20% above its initial value, the equilibrium temperature would then increase to 56°C, etc. These curves manifest the necessity to determine, to as large a degree as practical, the stability of the thermal control coatings when subjected to the space environment.

It can be seen in Fig. 10 that the satellite equilibrium temperature can be controlled over a range varying from about 15°C with an  $\alpha_s/\epsilon$  value of 1.0, to about 190°C with an  $\alpha_s/\epsilon$  value of 7.5. Therefore, by depositing the proper coating density on the satellite, any equilibrium temperature in the interval 15°-190°C can be obtained with Alodine 401-41 based on the experimental evidence obtained. Alodine 1200S would provide a smaller range of control and at a penalty of more weight.

**Application.**—Due to the commercial availability of Alodine 41 in the powder form only, an alternate, Alodine 45 was substituted to provide an all-liquid Alodine 401-45 for the Echo II application. This combination better lends itself to mass production processing where the liquids can be dispersed rapidly in solution for the purpose of maintaining the desired bath concentration. Since the 401-45 is better suited for large-scale application, it was selected for stability studies when exposed to a simulated space environment.

**Absorptance-Emittance Stability.**—Specimens of Echo II material coated with 185 mg/ft<sup>2</sup> of Alodine 401-45 were exposed to ultraviolet radiation in vacuum ( $< 10^{-6}$  torr), while being maintained at 0°, 25° and 50°C equilibrium temperature. This environment represents a simulation of the space environment to which the Alodine-coated material

would be subjected in space application. The vacuum was produced by an oil diffusion pump appropriately trapped to minimize backstreaming of oil vapors. The specimens were maintained at constant temperature by attaching them to a surface cooled by means of a temperature-controlled liquid-circulating bath. Ultraviolet radiation was provided by a General Electric B-H6 lamp, illuminating the specimens with about 2.5 times the energy present in the space solar spectrum in the interval 2000-4000Å. Other specimens of 401-45 were simultaneously exposed to the above-described environment except that the ultraviolet radiation was omitted. This permitted separation of thermal-vacuum-ultraviolet effects from thermal-vacuum effects.

The spectral absorptance of a specimen maintained at 0° in an ultraviolet-vacuum environment for 354 hr was found to increase by 40-170% at wave lengths less than 0.45μ, with much less effect at longer wave lengths (Fig. 11). As a result of these large effects, studies were made at other temperatures.

The spectral effects in the wave length interval 0.22-15μ resulting from 350 hr exposure at 50°C to the simulated environments are shown in Fig. 12(a) and 12(b). Fig. 12(a) shows the spectral absorptance of a specimen taken from laboratory stock compared with the same specimen after 350 hr exposure to the thermal-vacuum-ultraviolet environment. Fig. 12(b) shows the spectral absorptance of a similar specimen exposed simultaneously to the same thermal-vacuum environment containing no ultraviolet. It is noted in both cases that the absorptance increases in the interval 0.22-2.1μ and decreases in the interval 2.5-15μ. The thermal-vacuum-ultraviolet effects are greatest, particularly in the solar spectrum; however, the thermal-vacuum effects alone are by no means to be ignored. The changes of absorptance characteristics brought about by the thermal-vacuum exposure suggests the possibility that outgassing of the specimen may be appreciable. It will also be noted that the specimen maintained at 50°C in the simulated environment [Fig. 12(a)] was affected much less than the specimen maintained at 0°C in the same environment (Fig. 11). This, too, suggests the possibility of an outgassing phenomenon since, generally, rate of outgassing is strongly dependent on the specimen

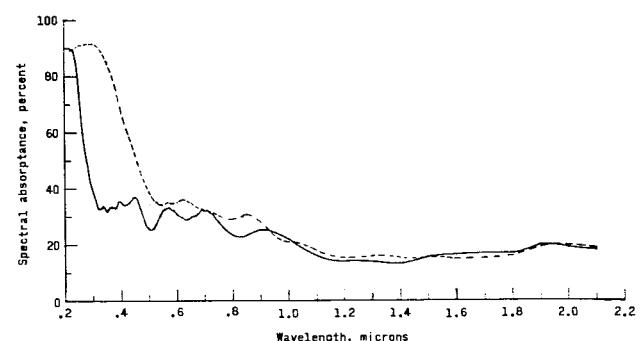


Fig. 11. Spectral absorptance effects due to 354 hr exposure to simulated thermal-vacuum-ultraviolet space environment: — before environmental exposure, - - - after environmental exposure. Test environment: pressure  $\approx 10^{-6}$  torr, specimen temp = 0°C, ultraviolet  $\approx 2.5$  suns.

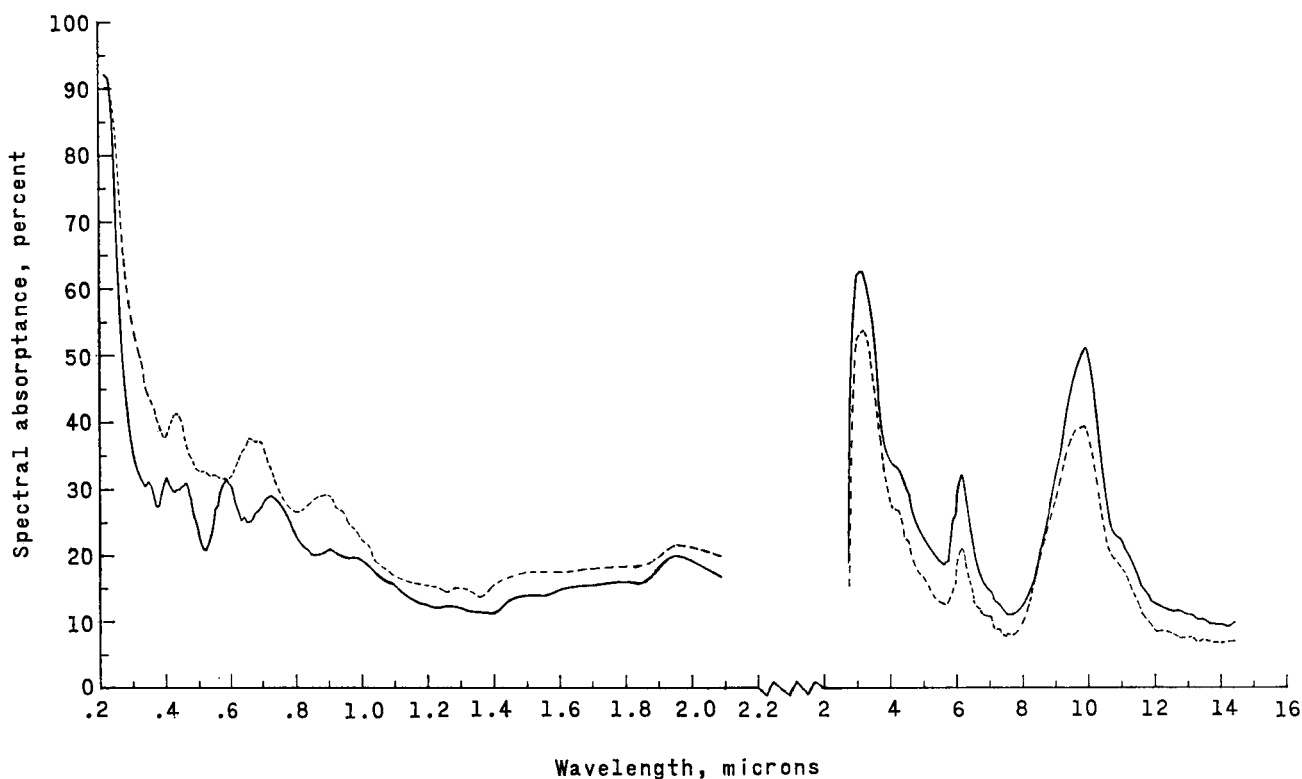


Fig. 12(a). Spectral absorbance effects due to 350 hr exposure to simulated thermal-vacuum-ultraviolet space environment: — before environmental exposure, - - - - after environmental exposure. Test environment: pressure  $\approx 10^{-6}$  torr, specimen temp =  $50^{\circ}\text{C}$ , ultraviolet  $\approx 2.5$  suns.

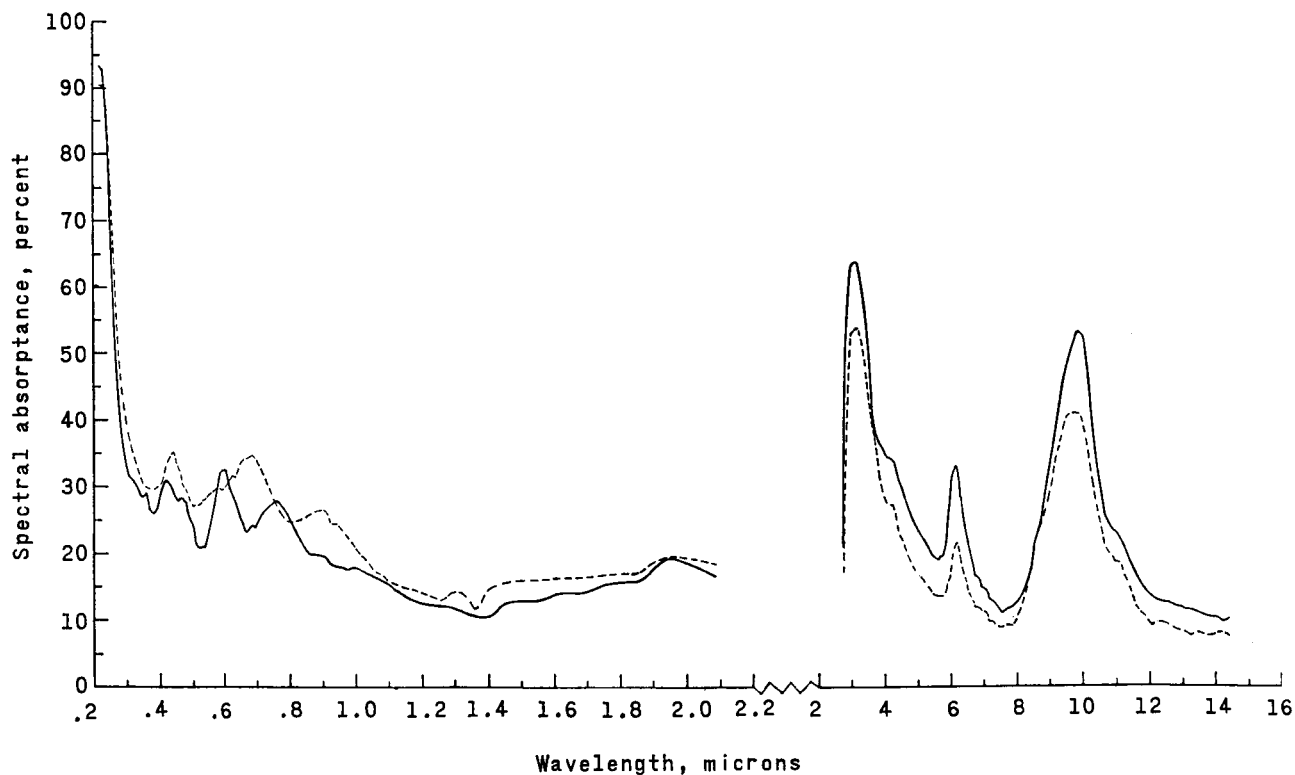


Fig. 12(b). Spectral absorbance effects due to 350 hr exposure to simulated thermal-vacuum space environment: — before environmental exposure, - - - - after environmental exposure. Test environment: pressure  $\approx 10^{-6}$  torr, specimen temp =  $50^{\circ}\text{C}$ , ultraviolet = zero.



temperature. In light of these findings, gas sorption (absorption and/or adsorption) and desorption (outgassing) studies were made in an endeavor at least to establish the presence of adsorbates by an independent method.

The desorption-sorption characteristics of the 401-45 coating were evaluated at ambient temperature (25°C) by the weight change technique. Two Ainsworth analytical balances, contained under bell jars, were used to monitor the specimen's weight continuously while cycling the pressure between atmospheric and 0.5 torr with one system and between atmospheric and  $10^{-6}$  torr with the other (Fig. 13). The weight changes are attributed entirely to the 401-45 coating in light of the fact that only 1.0 mg/ft<sup>2</sup> was lost from an uncoated specimen maintained in a vacuum of  $10^{-7}$  torr for 500 hr. The cycling of the environmental pressures of the two specimens was arranged so that desorption data could be attained at two distinct widely different vacuums and sorption data could be attained at atmospheric pressure in the presence of different gases. The amount of sorption that takes place after exposure to vacuum was found to be dependent on both the previous degree of outgassing and the type of gas to which it is exposed during sorption. Of the gases tested, the coating is most susceptible to sorption of air containing water vapor and least

susceptible to sorption of helium with dry air intermediate. To determine the effects of the sorbates present on laboratory stock, specimens were spectrophotometrically scanned in the interval 0.22-15 $\mu$ , then maintained in a vacuum of 0.5 torr for 280 hr at 25°C and scanned again before placing them in the simulated space environment at 25°C for 385 hr [Fig. 14(a) and 14(b)]. (A vacuum of 0.5 torr at 25°C was selected as the outgassing environment because spacecraft of the Echo type are usually maintained at these conditions in preparation for and during launch to satisfy inflation requirements.) It is noted that only slight changes of absorptance in the ultraviolet spectrum result from 0.5-torr outgassing. However, the absorptance bands are shifted considerably throughout the visible and near infrared. The subsequent 385 hr of thermal-vacuum-ultraviolet environment causes increased absorptance in the ultraviolet, some disturbance of band structure in the visible and further decrease of absorptance in the near infrared to 5 $\mu$ , beyond which the effect reverses and the absorptance increases back toward its original value [Fig. 14(a)]. It is noted in Fig. 14(b) that the effects of 0.5 torr and 25°C for 280 hr are increased by subsequent exposure to the simulated thermal-vacuum environment with little effects observed in the ultraviolet, very little spectral shift of the band structure in

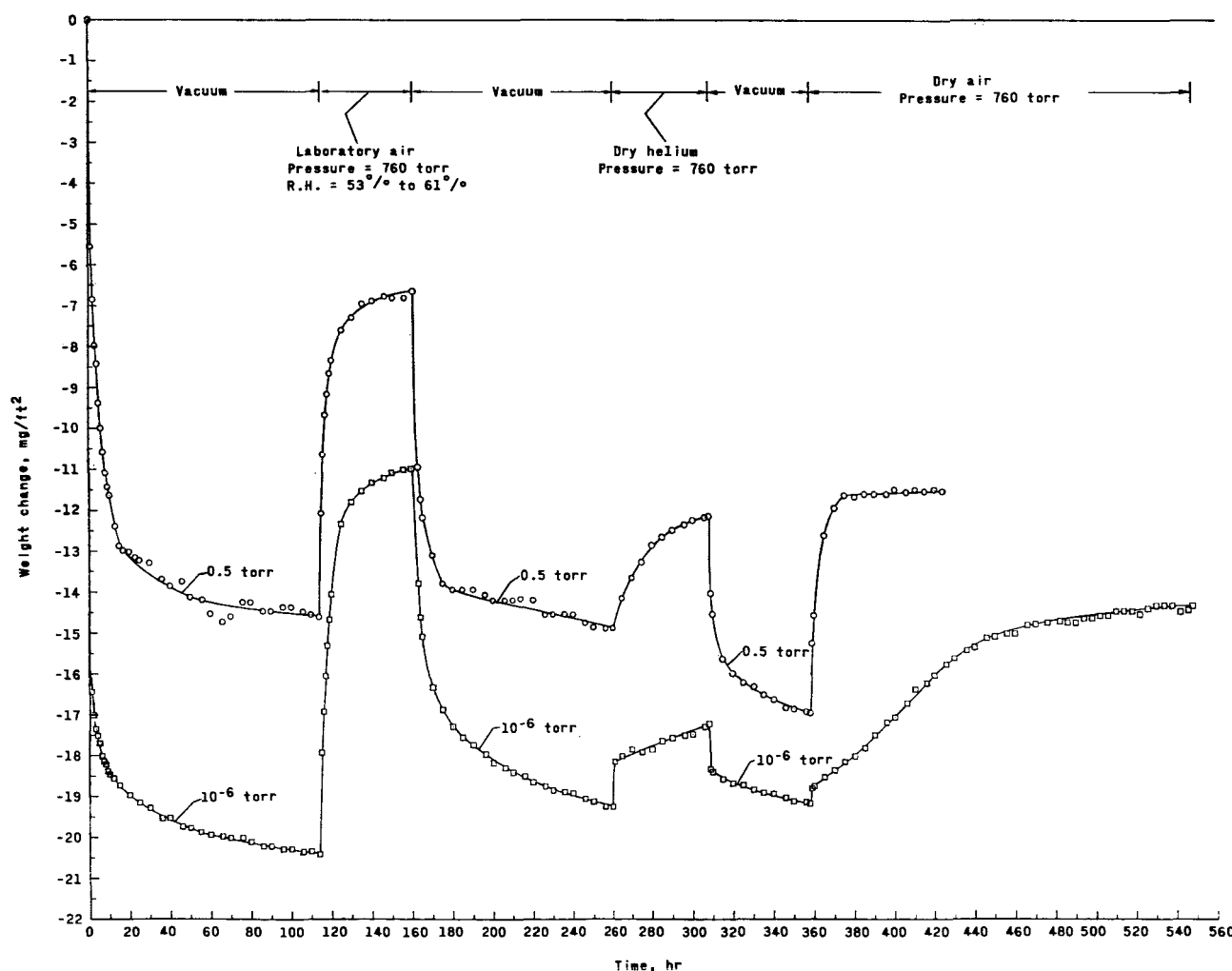


Fig. 13. Sorption characteristics of Alodine 401-45 at 0.5 torr and  $10^{-6}$  torr in the presence of wet air, helium and dry air.

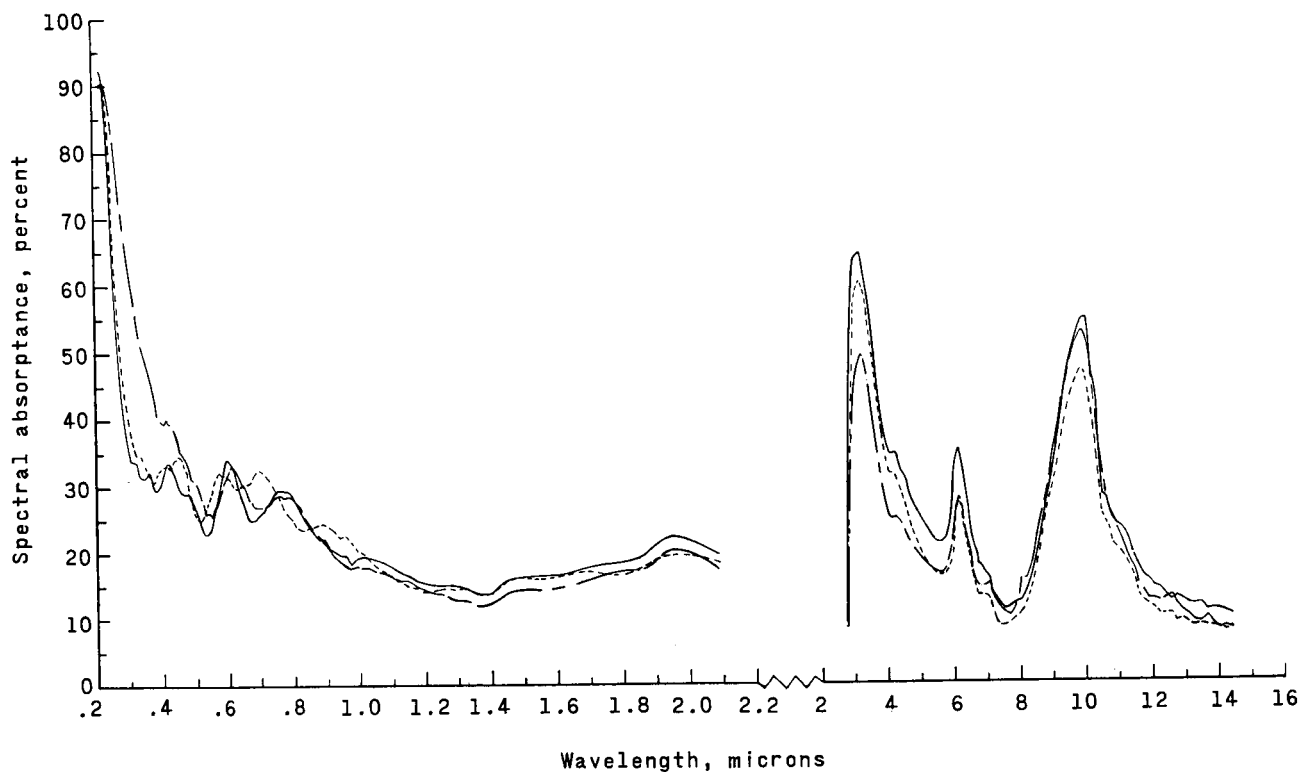


Fig. 14(a). Spectral absorbance effects due to 0.5 torr at 25°C for 280 hr and subsequent exposure to simulated thermal-vacuum-ultraviolet space environment for 385 hr: — before environmental exposure, - - - after 280 hr at 0.5 torr, — — after 385 hr environmental exposure. Test environment: pressure  $\approx 10^{-6}$  torr, specimen temp = 25°C, ultraviolet  $\approx 2.5$  suns.

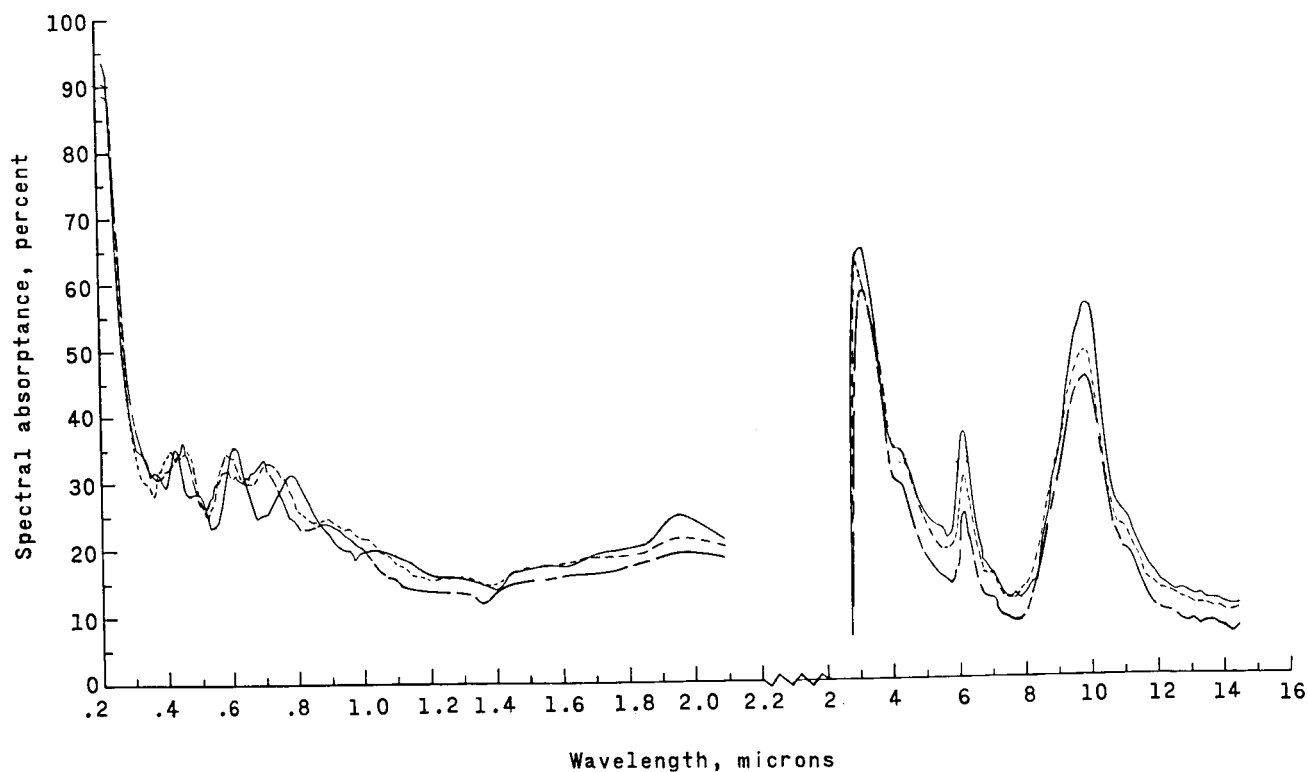


Fig. 14(b). Spectral absorbance effects due to 0.5 torr at 25°C for 280 hr and subsequent exposure to simulated thermal-vacuum space environment for 385 hr: — before environmental exposure, - - - after 280 hr at 0.5 torr, — — after 385 hr environmental exposure. Test environment: pressure  $\approx 10^{-6}$  torr, specimen temp = 25°C, ultraviolet = zero.

going from low vacuum to high vacuum and the amplitude of the absorptance bands is decreased in the infrared. There is no reversal effect in going from  $0.5$  to  $10^{-6}$  torr observed in the  $10\text{-}\mu$  band as had occurred in the presence of ultraviolet radiation [Fig. 14(a)].

The effects of these instability characteristics on the temperature control of Echo-type satellites can be more clearly illustrated by use of the total solar absorptance ( $\alpha_s$ ) as determined from Eq. [3] and the total normal emittance as determined from Eq. [6]. Due to the spectral limitations of the data, especially in the infrared where only about 50% of the energy radiated from a  $300^\circ\text{K}$  body is included between  $2.5$  and  $15\mu$ , instability will be discussed in terms of percentile change from its laboratory stock characteristic to that resulting from various environmental exposures. Mathematically, the per cent change in solar absorptance and emittance discussed herein is expressed as

$$100 \left( \frac{\alpha_{s,2} - \alpha_{s,1}}{\alpha_{s,1}} \right) \quad 0.22 \leq \lambda(\mu) \leq 2.1$$

and

$$100 \left( \frac{\epsilon_{N,2} - \epsilon_{N,1}}{\epsilon_{N,1}} \right) \quad 2.5 \leq \lambda(\mu) \leq 15$$

where the subscripts 1 and 2 refer to the specimen characteristics when taken from laboratory stock and that obtained after environmental exposure, respectively. The effects of environmental exposure periods up to 500 hr are included in Fig. 15 where equilibrium temperatures of  $0^\circ$ ,  $25^\circ$  and  $50^\circ\text{C}$  were maintained. Each specimen was removed from the environmental chamber and remained at atmospheric pressure no more than 2 hr before the second scan was made. The specimens were maintained at ambient temperature ( $25^\circ\text{C}$ ) during scan. Straight lines have been faired between each data point for convenience. However, the initial changes probably occur logarithmically rather than linearly as evidenced by the rapid outgassing of the specimen (Fig. 13). The specimens exposed to the thermal-vacuum-ultraviolet environment (solid curve) approach, somewhat asymptotically, a solar absorp-

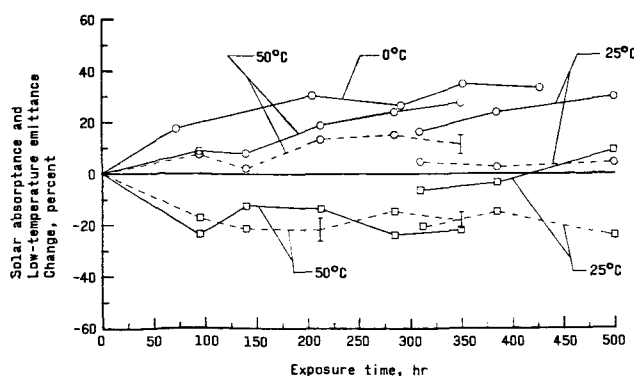


Fig. 15. Changes in solar absorptance ( $\alpha_s$ ) and low-temperature emittance ( $\epsilon$ ) resulting from exposure to various simulated space environments:  $\circ$  solar absorptance;  $\square$   $300^\circ\text{K}$  emittance,  $3 \leq \lambda(\mu) \leq 15$ ; — thermal-vacuum + ultraviolet ( $\approx 2.5$  suns); - - - thermal-vacuum. Test environment: pressure  $\approx 10^{-6}$  torr, specimen temp = as noted.

tance increase of 30% at a rate dependent on the specimen temperature. The same specimens decreased in emittance less than 25%. The specimens exposed to the thermal-vacuum environment (dashed curve) had an increase of solar absorptance not exceeding 15% while the emittance of these specimens decreased  $20 \pm 5\%$  within 100 hr and remained stable within these limits throughout the remaining 400 hr of exposure. These changes (Fig. 15) can be considered representative of those that would occur if Alodine 401-45 were used as the outside coating of a spacecraft that was exposed to ground level ambient conditions prior to launch.

Prelaunch environmental conditions necessary for Echo-type spacecraft are rather unique in that the folded structure is contained inside a vacuum of about 0.5 torr for periods ranging from weeks to months. This provides a significantly different thermal control surface in that the adsorbates will, to a large extent, be outgassed before the surface is exposed to the space environment. To simulate this history of events, specimens were taken from laboratory stock and spectrophotometrically scanned, as Fig. 14(a) and 14(b), then placed inside a vacuum of 0.5 torr for 280 hr before exposing them to their respective simulated space environment. To minimize sorption of atmospheric constituents after vacuum outgassing, the specimens were exposed to the atmosphere for periods less than 15 min during each spectral analysis. The spectral absorptance change of these specimens was significantly less than for those not outgassed before exposure to ultraviolet radiation. The absorptance resulting from thermal-vacuum-ultraviolet had a maximum increase of 10% during 375 hr (about 40 days sunlight in orbit) exposure and the thermal-vacuum effects remained less than 4% increase (Fig. 16). The emittance due to thermal-vacuum-ultraviolet decreased 22% during the first 100 hr and increased back toward its original value thereafter being about 5% down at the end of 375 hr. The thermal-vacuum environment caused an emittance decrease of  $20 \pm 5\%$  within 100 hr and remained within these limits thereafter.

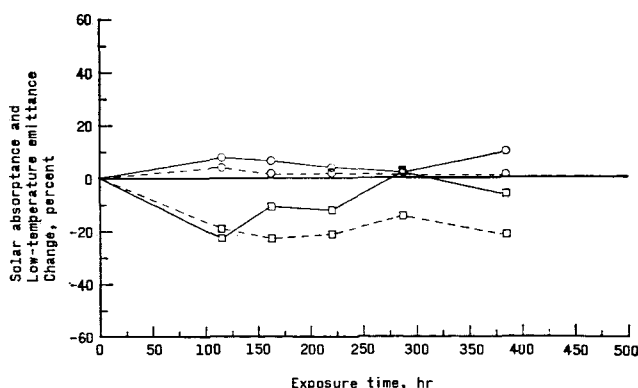


Fig. 16. Changes in solar absorptance ( $\alpha_s$ ) and low-temperature emittance ( $\epsilon$ ) resulting from exposure to simulated space environment after specimen outgassing at  $25^\circ\text{C}$  in 0.5 torr vacuum for 280 hr:  $\circ$  solar absorptance;  $\square$   $300^\circ\text{K}$  emittance,  $3 \leq \lambda(\mu) \leq 15$ ; — thermal-vacuum + ultraviolet ( $\approx 2.5$  suns); - - - thermal-vacuum. Test environment: pressure  $\approx 10^{-6}$  torr, specimen temp =  $25^\circ\text{C}$ .

### Conclusions

The investigation of the thermal radiation characteristics of amorphous phosphate coatings applied by chemical conversion of the surface has indicated that  $\alpha_s/\epsilon$  ratios of 1080 aluminum foil can be made to vary over the range 7.5-0.82 by controlling the surface density of the coating. The surface density of two such coatings, Alodines 401-41 or 401-45, required to control the temperature of the Echo II satellite to 55°C while in a continuous-sunlight orbit is about 200 mg/ft<sup>2</sup>.

The coating has outgassing characteristics such that about 11% of the coating, by weight, will be desorbed in a vacuum of  $10^{-6}$  to  $10^{-7}$  torr maintained at a temperature of 25°C within a period of 100 hr. This weight will be wholly or partially regained on re-exposure to atmospheric pressure depending on the gases and vapors present, exposure time, temperature and the extent of previous outgassing.

Thorough outgassing of this coating before launching it into space is beneficial for two reasons in Echo-type satellite application: first, it will provide more stable thermal radiation characteristics during exposure to the sunlit space environment and, second, it will eliminate undesirable temperature-dependent pressure fluctuations inside the vacuum-tight canister enclosing the folded spacecraft. The ultraviolet effects on solar absorptance ( $\alpha_s$ ) can be reduced from 30 to 10% by outgassing the coating before exposure to space ultraviolet radiation. The molecular structure of the coating is apparently altered when exposed to ultraviolet radiation in the presence of loosely attached adsorbates. The emittance will decrease about 20% below ambient values as a result of thermal-vacuum and/or thermal-vacuum-ultraviolet exposure attributable almost entirely to outgassing. As outgassing nears completion, the ultraviolet radiation will cause the emittance to increase back toward its original value while the surface not exposed to ultraviolet radiation will remain down in emittance  $20 \pm 5\%$ .

For application on the outside surface of an Echo-type satellite, prediction of the space environmental effects is that the equilibrium temperature would first increase and later decrease. Based on an initial design temperature of about 55°C, the space environmental effects should cause an initial increase of 10°-25°C during the first few days. The amount of temperature change will depend on the extent of outgassing before launch into orbit. After the first few days, the temperature should return toward its initial value differing by no more than 10°C after 2 months in a continuously sunlit orbit.

Manuscript received by ECS June 22, 1962; assigned to ECT July 12, 1962; revised manuscript received April 2, 1964. This paper was presented at the Los Angeles Meeting, May 6-10, 1962.

Any discussion of this paper will appear in a Discussion Section to be published in the Nov.-Dec. 1964 issue.

### REFERENCES

1. A. Douty and F. P. Spruance, Jr., "Amorphous Phosphate Coatings for Protection of Aluminum Alloys and for Paint Adhesion", 36th Annual Proceedings of the American Electroplaters' Society.
2. W. G. Camack and D. K. Edwards, "Effect of Surface Thermal Radiation Characteristics on the Temperature Control Problems in Satellites", in "First Symposium—Surface Effects on Spacecraft Materials", pp. 3-55, John Wiley & Sons, Inc. (1960).
3. G. A. Zerlaut, "Utilization of Pigmented Coatings for the Control of Equilibrium Skin Temperatures of Space Vehicles", Aerospace Finishing Symposium, Fort Worth, Texas, Dec. 8 and 9, 1959.
4. C. P. Butler and E. C. Y. Inn, "A Method for Measuring Total Hemispherical Emissivity of Metals", in "First Symposium—Surface Effects on Spacecraft Materials", pp. 195-211. John Wiley & Sons, Inc. (1960).
5. H. S. Allen and R. S. Maxwell, "A Text-Book of Heat", MacMillan and Co. Ltd. (1939).
6. E. R. G. Eckert, "Introduction to the Transfer of Heat and Mass", McGraw-Hill Book Co., Inc. (1950).
7. D. L. Clemmons, Jr., "The Echo I Inflation System", NASA TN D-2194.